



Synthesis of CoMo-based carbon hydrodesulfurization catalysts: Influence of the order of metal impregnations on the activity

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ABSTRACT

Series of CoMo-based carbon catalysts were synthesized via the successive impregnation method, in which the carbon material was impregnated first with cobalt. The activity of the catalysts in the hydrodesulfurization of dibenzothiophene using a high pressure batch reactor operating at 340 °C under 3 MPa of hydrogen was investigated. In general, the carbon-supported CoMo catalysts synthesized by the successive impregnation method (in this case cobalt was the first to be introduced) showed higher hydrodesulfurization activities for dibenzothiophene than the reference CoMo-based carbon catalyst prepared by the conventional successive impregnation. The remarkable hydrodesulfurization activities of these CoMo-based carbon catalysts are suggested to be a consequence of forming a new synergy between molybdenum and cobalt. The data provide evidence that the CoMo-bimetallic synergy is affected by the nature of the support and by the order of metal impregnation. The results support the view of the electronic origin of such synergy.

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1. Introduction

Molybdenum sulfide-based alumina catalysts [1,2] are mostly used in hydrotreating reactions. Alumina as a support is widely used in most commercial hydrodesulfurization (HDS) catalysts, because it has outstanding textural and mechanical properties and it is relatively cost-effective. The support is used principally to achieve better catalyst dispersion, which consequently increases the catalytic performance. Inclusion of promoters such as cobalt and nickel into the molybdenum-based catalyst improves greatly the catalytic activity of the catalysts in HDS reactions. Despite their long history of application, these catalysts are still plagued with some unidentified properties, notably unknown reactions of the supports with the metal components to form catalytically active and/or inactive species, and as yet not totally understood synergy between the base metals and the promoters.

Because of the strict rules widely adopted in developed countries to adjust the sulfur content in the middle distillate fuels to extremely low values [3–5], a new catalyst with an enhanced breakthrough activity is required. The interest in CoMo- and NiMo-based catalysts originates from the fact that such catalysts have been proven to exhibit thus far most of the prerequisite performances needed for their industrial application in hydro-treatment reactions. However, the task of developing a suitable

catalyst should be pursued further in regard to certain aspects. Thus, cobalt and/or nickel act as catalyst promoters, but the nature of such promotion is not yet fully understood. Catalyst synthesis in general is a fine art and delicate process, which involves many variable parameters that greatly influence the catalyst characteristics and hence their operation. Impregnation is the most common and broadly used method for catalyst preparations. In literature [6–8], it has been shown that the successive metal impregnation technique, in which the support is impregnated first with the molybdenum precursor and then followed by cobalt and/or nickel, is the preferred synthesis route to produce a catalyst of higher HDS activity. This trend was early on noted for alumina-supported CoMo catalysts [6–8]. Many studies [9–15] on the synthesis of supported CoMo catalysts most often utilize the successive impregnation method, in which the addition of molybdenum precedes that of cobalt. The outcome of the structural studies of the CoMo- and/or NiMo-based catalysts is limited; however, some indicative data could be obtained [6,9,16,17]. The influence of the order of impregnation in the preparation of cobalt- and molybdenum-based catalysts on their catalytic performance in HDS reactions has been studied in the literature only rarely. Carbon shows some advantages and interesting properties when compared to alumina as a support for CoMo catalysts. Among these advantages are the possibility of easily recovering the active metals from the spent catalysts, and the weak interaction found between carbon and the catalytic metals [9]. In a previous study [18], it was noticed further that the CoMo-based carbon catalysts possess dual

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Table 1
Textural characteristics of the active carbon

S_{BET}	1360 m ² /g
$S_{\text{t-plot}}$	1283 m ² /g
Micropore volume (t-plot)	0.03 cm ³ /g
Micropore area (t-plot)	77 m ² /g
External surface area	1283 m ² /g
BJH pore volume	3 cm ³ /g
BJH average pore size	9 nm

characteristics of being active hydrotreating catalysts as well as efficient adsorbents for the refractory sulfur containing compounds. Carbon alone has also been proven to exhibit a significant adsorption ability towards the sulfur containing compounds [19]. CoMo-based carbon catalysts have been reported to exhibit higher activity than the commercial CoMo-based alumina catalyst [9,19–23]. Furthermore, CoMo-based carbon catalysts might be less susceptible to coking, poisoning, and fouling than the CoMo-based alumina catalysts. In general, heterogeneous catalysts are made up of two main phases, the support and the metals. The research in novel potential HDS catalysts is devoted to the development of either of these two phases. The objective of this paper is to synthesize various CoMo-based carbon catalysts by changing the order of impregnation of molybdenum and cobalt and to test the activity of the catalysts in HDS of dibenzothiophene (DBT). DBT was chosen to represent the refractory sulfur containing compounds found in the middle distillate fuels. Interest was paid to address the question of whether molybdenum may act as a promoter for the cobalt-based carbon catalysts.

2. Experimental

2.1. Materials

All chemicals used in this study were of high purity grade and were obtained from Wako Chemical Co. The active carbon was purchased from Mitsubishi Chemical Co. and was used without further treatment. The physical texture of this activated carbon was determined by measuring the adsorption isotherm of nitrogen using an ASAP 2010 sorptomatic apparatus. The BET surface area was found to be 1369 m²/g with a pore volume of 3.1 cm³/g and a pore size of ~9 nm. The summary of the adsorption-derived parameters is presented in Table 1.

Table 2
Catalyst preparation, composition and references

Catalyst reference	First metal precursor introduced	Mo ^a (wt%)	Co ^b (wt%)	Co/[Co + Mo] atomic ratio	Method
C-5	Co	–	5	–	I
C-10	Co	–	10	–	I
M-10	Mo	10	–	–	I
CM-5 catalysts:					
CM-5-5	Co	5	5	0.62	II
CM-5-10	Co	10	5	0.45	II
CM-5-12	Co	12	5	0.40	II
CM-5-15	Co	15	5	0.35	II
CM-10 catalysts:					
CM-10-2	Co	2	10	0.89	II
CM-10-3	Co	3	10	0.84	II
CM-10-4	Co	4	10	0.80	II
CM-10-5	Co	5	10	0.77	II
CM-10-6	Co	6	10	0.73	II
MC-10-2	Mo	10	2	0.25	II
CM-15-5	Co	5	15	0.83	II

^I Impregnation.

^{II} Successive impregnation with sulfidation in between.

^a Molybdenum acetylacetonate.

^b Cobalt acetylacetonate.

2.2. Catalyst synthesis

2.2.1. Carbon-supported cobalt sulfide and/or molybdenum sulfide catalysts

Co/C and Mo/C catalysts with a cobalt content of 5 wt% and a molybdenum content of 10 wt%, respectively, were prepared by impregnation of the active carbon with an alcoholic solution of cobalt acetylacetonate and molybdenum acetylacetonate. The impregnated slurry was exposed to ultrasonication for 30 min. Then, the sample was dried at 70 °C in air using a rotary evaporator and thereafter overnight at 110 °C in vacuum. Prior to analysis, the sample was sulfided in a flow of 10% (v/v) H₂S in H₂ gas at a rate of 100 SCCM at 400 °C with space velocities (SV) of 100–250 min^{−1}. A plug-flow quartz reactor was used for this purpose. After the predetermined sulfidation time had elapsed, the gas was changed to argon, which was allowed to flow at 400 °C for 30 min. The argon gas was continually streamed over the sample while the sample cooled to ambient temperature. The Co/C and Mo/C catalysts, after sulfidation, are denoted as C-5 and M-10, respectively.

2.2.2. Carbon-supported CoMo catalysts, 5 and 10 wt% cobalt-based series

Two series of carbon-supported CoMo catalysts, CM-5 and CM-10, were synthesized by the successive impregnation method, in which the cobalt precursor was loaded first. First, the carbon was impregnated with an alcoholic solution of cobalt acetylacetonate. The slurry was exposed to ultrasonication for 30 min. Thereafter, the sample was dried in air at 70 °C and subsequently overnight at 110 °C in vacuum. The dried sample was subjected to sulfidation at 400 °C with a flow of 10% (v/v) H₂S in H₂ gas at a rate of 60 SCCM for 4 h with SV of 60–150 min^{−1}. The resulting material was impregnated further with an alcoholic solution of molybdenum acetylacetonate and treated systematically as mentioned above. The cobalt content in all samples of CM-5 series was fixed at 5 wt% and the molybdenum content varied from 5–15 wt%. However, the cobalt content in CM-10 series was maintained in all samples at 10 wt%, while the molybdenum content varied from 2–6 wt%. The CM-5 and CM-10 catalysts, after sulfidation, are denoted as CM-5-5,10,12,15 and CM-10-2,3,4,5,6, respectively, where the first number refers to the wt% of cobalt and the second number refers to the wt% of molybdenum. One catalyst coded as CM-15-5 was synthesized following the previously described procedure but with a cobalt wt% of 15 and molybdenum wt% of 5.

2.2.3. Carbon-supported CoMo catalyst, conventional order of impregnation

A carbon-supported CoMo catalyst (10 wt% Mo and 2 wt% Co) was prepared by the conventional successive impregnation method, in which carbon was impregnated first with an alcoholic solution of molybdenum precursor. The slurry was exposed to ultrasonication for 30 min and the solvent was evaporated in a water bath at 70 °C. The sample was dried overnight at 110 °C in vacuum. The residue was subjected to sulfidation treatment by flowing 10% (v/v) H₂S in H₂ gas at a rate of 60 SCCM with SV of 60–150 min⁻¹. This sulfided precursor was impregnated with an alcoholic solution of the cobalt acetylacetonate. The solution was exposed to ultrasonication for 30 min, followed by evaporation in air at 70 °C. Then, the sample was dried overnight at 110 °C in vacuum. Finally, the sample was sulfided at 400 °C in a flow of 10% (v/v) H₂S in H₂ gas for 3 h. While the temperature was maintained, the sulfiding gas was replaced with argon gas that was kept streaming for 30 min. The catalyst was denoted as MC-10-2. All synthesized catalysts were transferred after sulfidation to a desiccator until further use. The catalysts' metal compositions and references are summarized in Table 2.

2.3. Point of zero charge (PZC)

In the present work, the PZC, the pH at which the net surface charge of a material is zero, were estimated by measuring the pH of the material slurries in deionized water. The values of the mass percentage of the solids in the slurry were in the range of 7–10%. Within this range, the dependence of pH on the mass percentage can almost be neglected [24–26]. The water–solid slurry of the investigated samples was first exposed to ultrasonication for 20 min and then kept for 1 day for equilibration to take place before any pH measurements were carried out. The PZC values of the carbon and of the cobalt- or molybdenum-supported carbon catalysts (in the sulfided form) were estimated.

2.4. Catalytic activity measurements

The catalytic activity was investigated in a batch system at high pressure. A 100 mL magnetically stirred micro-autoclave reactor was utilized in all the investigations. Prior to the activity test, the catalyst was freshly sulfided by passing a stream of 10% (v/v) H₂S in H₂ gas at a flow rate of 100 SCCM at 400 °C. Thereafter, the catalyst was flushed with a flow of argon gas for 20 min before being allowed to cool to ambient temperature. A solution of 1% DBT in decane was utilized as a model reaction substrate. The catalyst after sulfidation (0.1–0.3 g) and the substrate solution (15 mL) were loaded in situ using glove system under Ar atmosphere into the autoclave reactor along with copper and/or iron fine powders to avoid the interference that presumably exerted by the self-produced H₂S during the reaction. The reactor was purged five times with H₂ before setting the pressure at 3 MPa. All experiments were carried out at 340 °C under 3 MPa of H₂. To study the kinetics of the reaction, small aliquots were carefully withdrawn from the feedstock at time intervals. The reaction products were analysed by gas chromatography in an Agilent 6890 equipped with a capillary column (methylsiloxane, 0.32 mm × 50 m) and a flame ionization detector (FID). The products were identified by gas chromatography–mass spectroscopy (GC–MS, Agilent 6890GC–5973MSD) using a built in library and the comparison with standard compounds.

2.5. X-ray diffraction

Cobalt acetylacetonate was subjected to sulfidation by installing the powder in a quartz reactor. A stream of 10% (v/v) H₂S in H₂

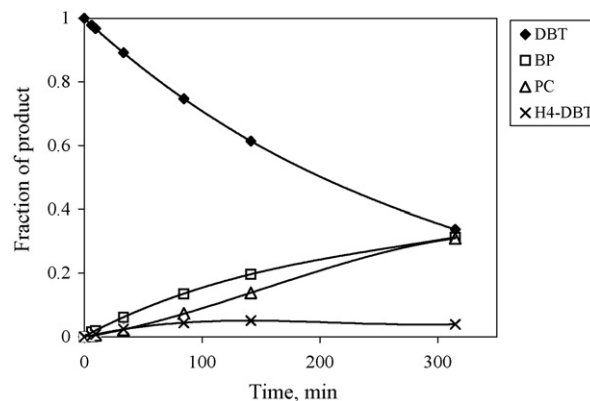


Fig. 1. Yield fractions as a function of reaction time for the DBT HDS over C-5 catalyst; 340 °C under 3 MPa H₂.

gas at 400 °C was allowed to flow over the sample at a rate of 100 SCCM for 6 h. The sulfiding gas mixture remained streaming over the sample, while the sample cooled to ambient temperature. The resulting phase was characterized by X-ray powder diffraction analysis on a Rigaku Geiger Flex Diffractometer using Cu K α radiation ($\lambda = 1.542 \text{ \AA}$).

3. Results and discussion

3.1. Catalytic activity in the HDS of DBT

DBT and its derivatives are among the most important refractory sulfur containing compounds in the middle distillate fuels. The HDS of such compounds have been widely screened to evaluate the catalysts' activities [12,13,20]. In this study, the impact of the catalyst synthesis routes on the activity in the DBT HDS was investigated. The observed HDS products at the prescribed reaction conditions over all the present catalysts were exclusively biphenyl (BP), phenylcyclohexane (PC) and 1,2,3,4-tetrahydrodibenzothiophene (H4-DBT). The plots of the DBT transformation as a function of time for C-5, M-10, CM-5-10 (example of CM-5 series), and MC-10-2 catalysts are represented in Figs. 1–4, respectively. The DBT HDS reaction over all catalysts fitted reasonably pseudo-first-order kinetics with respect to DBT, with a regression parameter of >94%. Figs. 5 and 6 depict the pseudo-first-order plots of the DBT HDS over CM-5-10, CM-10-5, and C-5 and M-10 catalysts. The apparent kinetic results of the activity and selectivity of the catalysts in this study are summarized in Table 3. The results show that the reaction proceeds via the involvement of two parallel-consecutive reactions

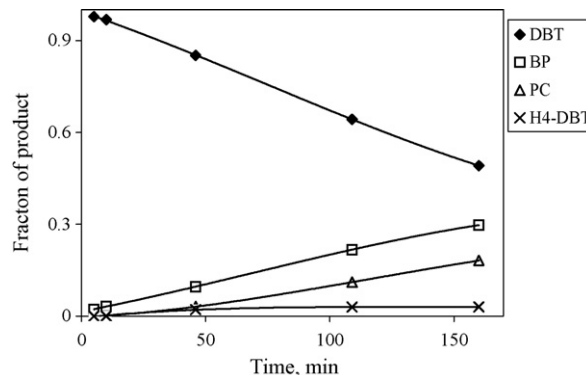


Fig. 2. Yield fractions as a function of reaction time for the DBT HDS over M-10 catalyst; 340 °C under 3 MPa H₂.

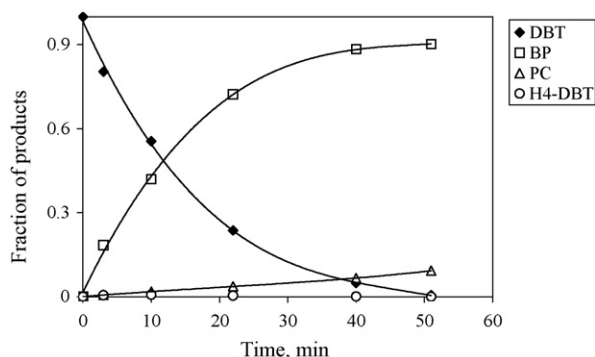


Fig. 3. Yield fractions as a function of reaction time for the DBT HDS over CM-5-10 catalyst; 340 °C under 3 MPa H₂.

namely, direct desulfurization (DDS), which yields biphenyl, and hydrogenation (HYD), which yields 1,2,3,4-tetrahydrodibenzothiophene as an intermediate that reacts further to produce phenylcyclohexane. It is interesting to note that in C-5 and M-10 catalysts, the contribution from the HYD pathway was as significant as that from the DDS pathway. The M-10 catalyst was slightly more active than the C-5 catalyst. For all catalysts except, C-5 and M-10, it could be observed that the reaction proceeds with a predominant contribution from the DDS pathway. However, the activity of the MC-10-2 catalyst is much lower than that of the CM-15-5 catalyst and the catalysts in either the CM-10 or CM-5 series. Furthermore, the CM-5 catalysts showed significant higher catalytic activities than the CM-10 catalysts.

The method used for the synthesis of the catalyst is regarded to be the most important parameter determining the characteristics of potentially active sites produced. The catalysts most commonly applied in the HDS reactions are derived from alumina-supported oxides of cobalt and molybdenum, which are usually sulfided in operation. A successive impregnation, where molybdenum is loaded first followed by cobalt has been reported to be the best route in obtaining highly active catalysts. Thus, such sequence of metal loading seems to be crucial in producing effective active sites [6,7]. Interestingly, most studies have recognized this order of metal impregnation as fundamental to any synthesis of CoMo catalyst. Obviously, a catalyst's synthesis may involve a large number of independent variables in the procedure, where every aspect should be considered carefully. The effect of the synthesis parameters of CoMo catalysts on their HDS activity has been the subject of numerous studies [27–30]. In the present study, we focused on the effect of the order of metal impregnation of active carbon on the catalytic activity of the finished catalysts in the DBT

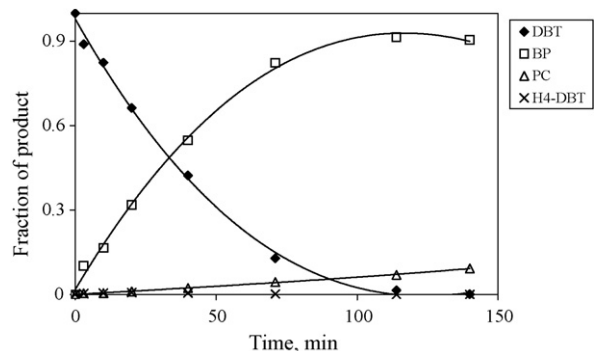


Fig. 4. Yield fractions as a function of reaction time for the DBT HDS over MC-10-2 catalyst; 340 °C under 3 MPa H₂.

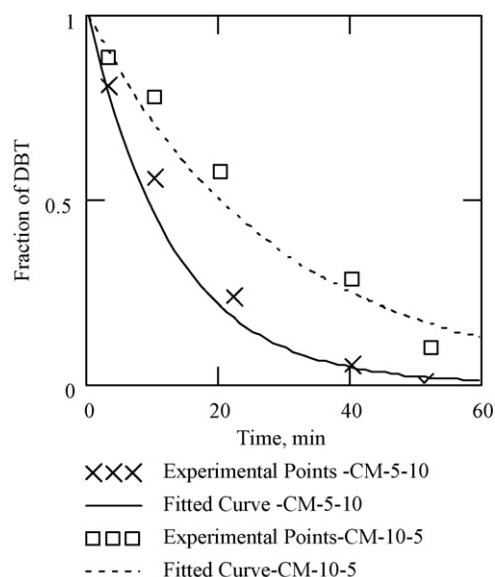


Fig. 5. Pseudo-first-order plots of the HDS of DBT over CM-5-10 and CM-10-5 catalysts.

HDS. The study was aimed to clarify, whether the order of loading in case using active carbon as a support is of importance.

The catalytic activities of the present catalysts are based on the determined apparent pseudo-first-order rate constants. MC-10-2 catalyst was synthesized according to the conventional successive impregnation, in which molybdenum was loaded first. This catalyst was used as a reference for the other catalysts prepared in this study. The catalysts of the CM-10 and CM-5 series showed a higher activity by an order of magnitude when compared to that of the MC-10-2 catalyst in the DBT HDS. The HDS activity of the carbon-supported CM catalysts usually goes through a maximum as the molybdenum loading increases. The maximum value, however, is dependent on the cobalt weight percent. Cobalt- and/or molybdenum-based carbon catalysts have little HDS activities as shown in Table 3. When comparing the catalytic activity of the CM-10 and CM-5 series with

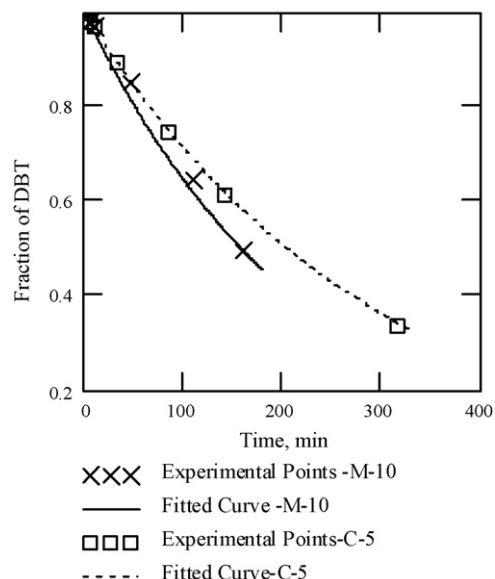


Fig. 6. Pseudo-first-order plots of the HDS of DBT over C-5 and M-10 catalysts.

Table 3

Apparent activity and selectivity of CM-5-x and CM-10-x catalysts in the HDS of DBT; 340 °C and 3 MPa of H₂

Catalyst	Activity (s ⁻¹ g _{cat} ⁻¹ 10 ⁻⁴)	Product distribution at fraction conversion of 0.5		
		Biphenyl (BP)	Phenylcyclohexane (PC)	H4-DBT
C-5	3	0.24	0.22	0.04
C-10	3	0.24	0.22	0.04
M-10	4	0.29	0.17	0.04
CM-5-5	339	0.48	0.02	0.01
CM-5-10	517	0.48	0.02	0.01
CM-5-12	444	0.48	0.02	0.01
CM-5-15	411	0.48	0.02	0.01
CM-10-2	109	0.48	0.02	<0.01
CM-10-3	133	0.48	0.02	<0.01
CM-10-4	147	0.48	0.02	<0.01
CM-10-5	278	0.48	0.02	<0.01
CM-10-6	117	0.48	0.03	<0.01
MC-10-2	150	0.48	0.02	<0.01
CM-15-5	265	0.48	0.02	<0.01

the sum activities of the M-10 and C-5 catalysts, a certain synergy between cobalt and molybdenum has to be proposed.

3.2. Influence of PZC

Catalyst carrier, when placed in an aqueous solution, is considered to act either as a cation exchanger or as an anion exchanger, according to the net charge on their surface. Thus, the PZC values can be taken as an index of the material propensity to become positively or negatively charged. In catalyst preparation, the adsorption of cationic and/or anionic complexes can be qualitatively predicted based on this characteristic. The PZC of the active carbon in the present study was ~6.1, which indicates that the carbon surface is slightly acidic and that in the slurry solution, the surface might be negatively charged. The pH of the molybdenum acetylacetonate/water system was 2.4. The pH of the cobalt acetylacetonate/water system was 7.7. On the other hand, the PZC values of the pre-sulfided C-5 and M-10 catalysts were 8.2 and 1.8, respectively. The estimated PZC values of the pre-sulfided carbon-supported 2, 10, and 15 wt% cobalt catalysts were 7.8, 8.1, and 8.3, respectively.

In light of the PZC results, the preferential order of impregnation can be discussed. Adsorption of cations is readily favored, when the PZC of the metal complex is higher than that of the support. The net charge on the surface of the present active carbon in aqueous media is negative so that the cations will be preferentially adsorbed. Accordingly, the cobalt cations, when loaded first, might be better dispersed on the surface of the present active carbon than the molybdenum anions, if firstly impregnated. Furthermore, the PZC values of the pre-sulfided cobalt-based carbon catalysts might allow better dispersion of the molybdenum anions. The slurries of the cobalt-based active carbon catalysts in water with 10 and 15 wt% cobalt content showed pH values that are typical for the cobalt-based active carbon slurry with 5 wt% cobalt content. This reveals that a formation of a monolayer cobalt phase is readily obtained at a loading of 5 wt% cobalt. More cobalt loading might more or less accumulate cobalt in agglomerates and hence lead to poor cobalt dispersion, and possibly leading to a multilayer adsorption. Therefore, a load of 5 wt% cobalt is proposed to be the optimum weight ratio that affords optimum dispersion of cobalt on the surface of this active carbon. This ratio is close to what Lee et al. have found but for Al₂O₃-supported CoMo catalyst

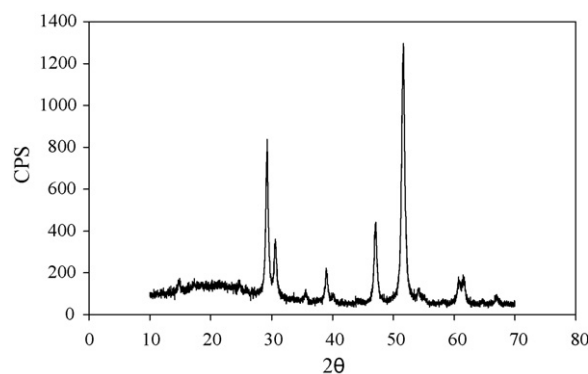


Fig. 7. XRD pattern of Co₉S₈ synthesized from sulfidation of cobalt acetylacetonate at 400 °C by 10% (v/v) H₂S in H₂ gas.

[30]. In terms of the PZC value, the present active carbon might behave in a different manner than alumina, which is generally characterized by high PZC values. However, the behavior of this active carbon appears to be comparable to that of silica which is well-known to possess low PZC values, i.e., <4 [31–33]. The HDS activity results of the catalysts in the present study are in agreement with the above mentioned phenomena. Catalysts in the series, where cobalt preceded molybdenum in the impregnation, exhibited the highest activities. This is partly a consequence of the catalyst dispersion that plays a vital role in the activity.

3.3. Catalyst phases

The XRD pattern, Fig. 7, of the cobalt phase produced from the sulfidation of cobalt acetylacetonate with 10% (v/v) H₂S in H₂ gas indicates the formation of a Co₉S₈ phase structure; all of the XRD peaks can be indexed in the Co₉S₈ phase (ASTM card number 13-364). Thus, the Co₉S₈ phase is supposed to be formed in case of the pre-sulfided cobalt-based carbon catalysts where it serves as a second support for the molybdenum phases. On the other hand, in a previous study [34], we have shown that the analogous sulfidation treatment of molybdenum acetylacetonate resulted in the formation of a MoS₂ phase, characterized by a low number of stacked MoS₂ layers. It is worthwhile to mention that with this sulfidation treatment, quantitative transformations, as determined by the gravimetric tool, to the prescribed metal sulfided phases were observed. The most generally accepted hypothesis in synthesis of an active CoMo-based catalyst is that sulfidation of molybdenum should precede that of cobalt and nickel, whereas the crystalline structure of the MoS₂ can serve as anchoring sites for the cobalt and nickel atoms. On the other hand, to investigate further, if the Co₉S₈ acts as a secondary support for molybdenum, sulfidation between successive impregnation steps with the metal complexes must be conducted. In the synthesis, all catalysts were subjected to two sulfidation steps with 10% (v/v) H₂S in H₂ gas, one at the end of the first impregnation stage and the second after the subsequent impregnation with the promoter. Thereby, the MoS₂ and Co₉S₈ phases are essentially assumed to exist on the surface of the carbon where Co₉S₈ is supposed to act as a secondary support for the MoS₂ phase. Therefore, the catalyst phases over the carbon support are threefold: the MoS₂, the Co₉S₈ and the new phase that results from synergies between the two former phases. The synergy may lead to the formation of a Co-Mo-S phase in which its catalytic efficiency may considered dependent on the order of metal impregnation. The catalytic activity is principally attributed to such synergy, because the activities of the other phases, when tested independently, were relatively low in agreement with those reported in literature [16,17].

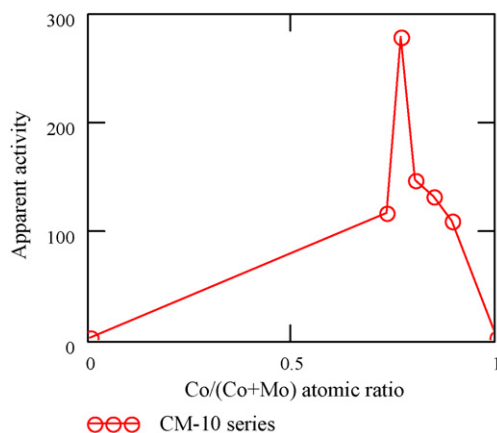


Fig. 8. Dependence of the HDS activity ($s^{-1} g_{cat}^{-1} 10^{-4}$) for DBT on the loading of the molybdenum in CM-10 catalyst series.

3.4. Influence of promoter loading on the HDS activity

Fig. 8 shows the correlation between the catalytic activity, expressed by the apparent pseudo-first-order rate constant, and the molybdenum loading in the CM-10 catalyst series. The CM-10-5 catalyst exhibited the highest activity in the DBT HDS reaction within this series. Fig. 9 shows the effect of molybdenum loading on the catalytic activity of the catalysts in the CM-5 series in DBT HDS when cobalt loading was held constant at 5 wt%. One may note the relative significant activity of all catalysts in this series. In general, the activities of catalysts of the CM-5 series in the transformation of DBT were much higher than those of the catalysts in the CM-10 series. The optimum cobalt load is very much associated with the ionic nature of the support, as discussed in Section 3.2. This revealed the importance of the monolayer cobalt species in HDS reactions. In the literature, it is reported that the maximum HDS activity is attained at a specific ratio of promoter to base metal, i.e., atomic ratio of cobalt (nickel) to molybdenum. However, the precise value of this ratio at which maximum activity has been reported differs somewhat from study to study. Typically, the promoter is added to achieve a Co/[Co + Mo] atomic ratio in the range of 0.3–0.4. So far, this is the most reported range of the metal atomic ratio, for which the CoMo-based catalysts have been found to exhibit optimum performance in HDS reactions [1,2,6,11,12]. Presumably, the type of catalyst support has no considerable effect on this range of Co/[Co + Mo] ratio. The observed atomic ratio of Co/[Co + Mo] in the CM-5 catalyst series, at which maximum DBT HDS activity was obtained, was ~0.45

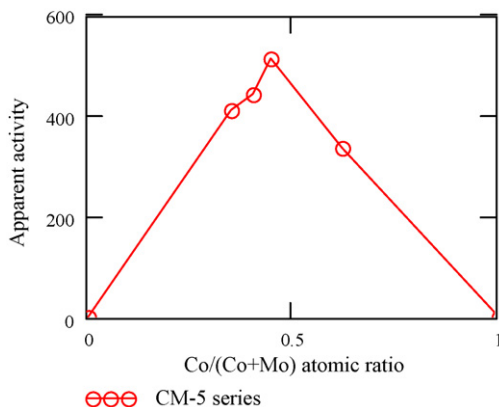


Fig. 9. Dependence of the HDS activity ($s^{-1} g_{cat}^{-1} 10^{-4}$) for DBT on the loading of the molybdenum for CM-5 catalyst series.

(slight upward shift from the above value for the conventional catalysts). This may emphasize the existence of an intrinsic correlation between the promoter, i.e., molybdenum and the metal, i.e., cobalt, regardless of the surface characteristics of the support. Interestingly, the synergy exists in the entire range of studied promoter to metal ratios, however, in different degrees. The CM-15-5 catalyst was synthesized with cobalt being impregnated first with a load of 15 wt%. Because the present active carbon possesses a high surface area, it was thought that a good dispersion of this amount of cobalt is still feasible. Nevertheless, the activity of the CM-15-5 catalyst in the DBT HDS reaction was little lower than that over any of CM-10-5 and CM-5-5 catalysts. This was in contrast to the above mentioned assumption, although there is evidence that there is still a considerable synergy between cobalt and molybdenum. Multi-layer cobalt species formation, as shown from the PZC results, could possibly be the cause of this lower activity. Three cobalt base loads were investigated. These are 5, 10 and 15 wt% Co. Catalysts with 5 wt% cobalt-based carbon promoted by molybdenum showed the highest activity. Thus, the effectiveness of the synergy depends on the support as well as on the Co/[Co + Mo] atomic ratio.

The results showed that the molybdenum might act as a promoter for the Co_9S_8 phase. One may further note that in the catalyst series with the best HDS activity, the cobalt weight ratio was 5 wt%, while the molybdenum weight ratio was in the range from 5 to 15. The remarkable activity associated with the high weight ratio of molybdenum is questionable. A crystal growth of the MoS_2 phase anchored to possibly a well-dispersed Co_9S_8 phase over carbon is suggested. In terms of the geometrical point of view, the resultant MoS_2 anchored crystals afford more exposure space to the substrate for better interaction. It seems that the electronic characteristics of the MoS_2 anchored to the Co_9S_8 plays also a key role at the surface. The results suggest that the activity is associated with a narrow range of critical crystallite sizes of the promoter.

3.5. Synergy between cobalt and molybdenum versus the HDS activity

Looking at the present results, it is interesting to note that the DBT HDS activities of the synthesized catalysts, in which cobalt was loaded first, were much more pronounced than the activity of the MC-10-2 catalyst, where molybdenum was loaded first. The results in Table 3 reveal that the synthetic methodology of impregnating carbon with cobalt, before impregnating it with molybdenum is an effective approach to potentially highly active HDS catalysts. In general, for the CoMo catalysts synthesized by the conventional successive impregnation method, where molybdenum was loaded first, followed by cobalt, a certain synergy between molybdenum and cobalt is achieved. It is known that the significant improvement in the catalytic activity resulting from the addition of the promoter originates from this synergy, in which the two components, promoter and base metal, interact together. Thus, it is a good approach to screen the catalysts according to the potential of such synergy.

The magnitude of the synergistic effect, SE, was determined according to the following equation:

$$SE = \frac{k_{CM}}{k_{C-5} + k_{M-10}}$$

where k_{CM} , k_{C-5} and k_{M-10} are the apparent pseudo-first-order rate constants of the CM-5 or-10, C-5 and M-10 catalysts, respectively.

Fig. 10 is a phase diagram that shows the relation between the synergetic value and the Co/[Mo + Co] atomic ratio for the catalyst series synthesized via the approach of loading cobalt first. Two peaks can be observed from this relation, one at a Co/[Co + Mo]

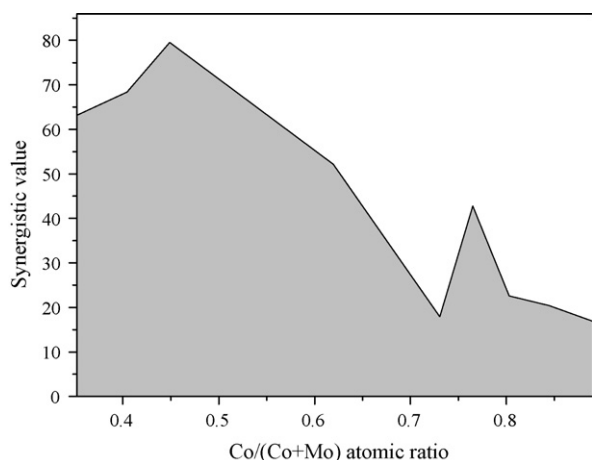


Fig. 10. Synergy effect exhibited by molybdenum and cobalt when supported on carbon for the DBT HDS.

atomic ratio of 0.45 and the other at 0.76. An optimum synergistic effect of about 80 was observed for the Co/(Mo + Co) atomic ratio of 0.45, i.e., for the CM-5-10 catalyst. Nevertheless, a significant synergistic value can still be noted for the other catalysts. Some of the present synergy effects are much higher than those reported in the literature for alumina and other active carbon-supported catalysts [13,35]. The synergy value for MC-10-2 catalyst was found to be much lower than that for the catalysts in the CM-10 and CM-5 series; however, it is still higher than that for the conventional CoMo-based alumina catalysts [13]. The catalysts in the latter series are an order of magnitude more active than the other studied catalysts.

Cobalt is added to molybdenum-based alumina catalysts to achieve a significant HDS activity. The promoting role of cobalt is associated with the presence of a certain synergy that forms the Co-Mo-S phase. However, such synergy was observed in supported and unsupported CoMo-sulfide catalysts. Studies on CoMo-based alumina catalysts revealed that the order of impregnation is important, where molybdenum loading first was found to result in more active catalysts in the HDS reaction as compared to when the reversed order of impregnation was employed. The order of the metal impregnation as well as the metal load ratio plays a key role in the potential of the resultant synergy. CoMo-based alumina catalysts, prepared by impregnating cobalt first, exhibited low synergy between cobalt and molybdenum, and accordingly low activity [6,7,36]. Two forms of Co-Mo-S phases, from which the synergy results, were assigned. These are designated type I, in which the molybdenum is not fully sulfided, so that some bridging oxygen ions between molybdenum and the support exist, and type II, in which the molybdenum is fully sulfided, so that the interaction between the active phase and the support is only due to van der Waals forces. The Co-Mo-S phase, type II, is more important in terms of the HDS activity. Basically, type II is exclusively obtained, when organic ligands are involved in the preparation (e.g., nitrilotriacetic acid, NTA) [11,28,29]. It was revealed that there is an interaction between the molybdenum phase and alumina and that as this interaction decreases, presumably via increasing the number of MoS₂ layers, it improves the catalyst activity through generating the Co-Mo-S phase of type II.

In the present study, a significant increase in the HDS activity was observed when cobalt was loaded first. The weak interaction between carbon and the metal catalysts may be crucial in this regard. While the synergy in the conventional cobalt promoted molybdenum-based alumina catalysts is mainly attributed to the

existence of Co-Mo-S phase type II, we speculate in light of the present study that such a concept may still be valid to discuss the present results. Thus, MoS₂ may decorate the Co₉S₈ phase in much the same manner as cobalt promotes MoS₂. However, the surface dependency of interaction between Co₉S₈ and MoS₂ has not yet been determined. Whether Co₉S₈ acts as a secondary support for molybdenum or whether, vice versa, MoS₂ acts as a secondary support for Co₉S₈ phase, the active phase results from the symmetrical interaction of the two phases. Such interaction has, however, attracted limited studies [37,38]. The synergistic phase Co-Mo-S is essential in creating the unsaturated active sites. The importance of the order of metal impregnation on the catalytic activity is highly dependent on the nature of the support. Cobalt and molybdenum sulfide phases are supposed to have no chemical interaction with the carbon support. This could probably be the reason that makes CoMo-based carbon catalysts more active than the corresponding CoMo-based alumina catalysts via facilitating the formation of the Co-Mo-S phase type II or a phase analogous to it. As the study in this area is just at its beginning, it is difficult to predict the optimum activity related to such synergy. This new synergy, i.e., due to Co-Mo-S phase, can contribute to the electronic character of the promoted active sites [39]. If this is the case, then the charge transfer between the Co₉S₈ and MoS₂ phases can occur irrespective of which phase is set to be the carrier for the other. The dispersion of the metal sulfide phase and the interaction with the support are obvious factors that help to determine the potential of the resultant synergy. Interestingly, the observed synergy between cobalt and molybdenum for CoMo-based carbon catalysts is of an order of magnitude higher than that reported for the conventional CoMo-based alumina catalysts (the synergistic effect mostly reported for alumina-supported catalysts falls in the range of 5–15) [1,13]. It is well established that a Co-Mo-S type II phase results, when weak interactions between molybdenum and alumina exist. When comparing the synergistic value found in the conventional CoMo-based alumina catalyst with the present catalysts, one may conclude that the new Co-Mo-S synergy may be more effective in creating unsaturated active sites than the Co-Mo-S synergy type II. A question may be addressed on how to interpret the low synergy between cobalt and molybdenum for CoMo-based alumina catalysts when prepared via the successive impregnation method, where cobalt is loaded first. A tentative answer may be that the cobalt precursor may be thought to have a strong interaction with the alumina (an example is the formation of the cobalt aluminate spinel, CoAl₂O₄), which accordingly affects the formation of the new phase [40]. Moreover, cobalt species deposited on alumina have been reported to be hardly sulfided in absence of molybdenum. Bad dispersion of the cobalt species on the alumina surface caused by the amphoteric nature of alumina may be another reason. More research utilizing the present method of preparation on other supports are needed and encouraged, as it will assist in assigning the electronic nature of the active sites in detail.

3.6. Effect of the order of metal impregnation on the DBT HDS selectivity

The product selectivities of the present catalysts in the DBT HDS reaction are included in Table 3. In such parallel-consecutive type reactions, one should be careful in dealing with the product distribution achieved at a variety of conversion levels. Appropriate comparison of catalyst selectivities should be based on a similar conversion level. Moreover, the product selectivities over the present catalysts are not significantly affected by either the impregnation order or the metal loading as shown from Table 3. The direct desulfurization route that leads to biphenyl is the most

predominant path. Thus, for the catalysts, in which cobalt was impregnated first, it is suggested that the reaction mechanism and the function of active sites remain unchanged, whereas either the number of the active sites or the potential of the active sites could be changed. Both M-10 and C-5 catalysts led to significant selectivities along the hydrogenation route in the DBT HDS. The results of the activity and the selectivity for M-10 and C-5 catalysts suggest that the nature of the active sites in these non-promoted catalysts might be different from that in the promoted catalysts. The selectivity results may also emphasize the importance of the electronic properties of the new metal-promoter interaction.

4. Conclusions

The order of impregnation (cobalt first, or molybdenum first) is a prominent parameter to achieve the optimum synergy and accordingly maximize the catalytic activity. Catalysts with cobalt loaded first (before molybdenum) on the carbon support, showed higher activity in the DBT HDS reaction than catalysts where molybdenum was loaded first. The advantage of this order of impregnation is a reflection of the better dispersion of the catalysts as explained by the PZC values of the active carbon and of the cobalt and/or molybdenum-based carbon slurries. The identity of the resulting synergy for the CM-catalysts seems to be different from those prepared by the normal synthesis route, where molybdenum impregnation precedes cobalt. New Co-Mo-S phase synergies are proposed to be present in the CM-5 and CM-10 catalyst series. A significant increase in the catalytic activity for the DBT HDS is achieved when the Co/[Co + Mo] atomic ratio is 0.45. The type of support and the arrangement of metal addition along with the metal weight ratio are speculated to be quite critical for assigning the efficiency of the resultant active sites. The results suggest that the produced synergies between the bimetallic CoMo catalysts could be many and of various dimensions. The study addresses an open argument of whether the resulting synergy phase due to reversing the normal order of metal impregnation contributes more to the catalytic activity than the classic Co-Mo-S phase would.

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